HREM studies of intergrowths in $Sr_2[Sr_{n-1}Ti_nO_{3n+1}]$ Ruddlesden-Popper phases synthesized by mechanochemical activation

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Abstract

A mechanochemical activation route has been applied in order to obtain the *n*=1-4 and ∞ members of the $Sr_2[Sr_{n-1}Ti_nO_{3n+1}]$ Ruddlesden-Popper series from different $(n+1)SrO:nTiO_2$ mixtures. The mechanosynthesis of $SrTiO_3$ and Sr_2TiO_4 was observed during the milling process from the initial stoichiometric mixture, but in the cases of the *n*=2-4 members, a subsequent thermal treatment was needed. The synthesis protocol of $Sr_3Ti_2O_7$ has been greatly improved and this compound can be isolated

as a single, crystalline phase after annealing at 800 °C. In the case of $Sr_4Ti_3O_{10}$ and $Sr_5Ti_4O_{13}$, the formation temperature was also decreased, but members with *n*=3 and 4 could not be isolated. Detailed investigations using electron microscopy methods (TEM, HREM and SAED) were carried out in the samples corresponding to *n*=2-4. Although a single ordered $Sr_3Ti_2O_7$ structure is dominant in the sample corresponding to *n*=2, a few intergrowths of other Ruddlesden-Popper phases were observed. In the cases of *n*=3 and 4, the intergrowths of Ruddlesden-Popper phases are more frequent than in the *n*=2 composition and are randomly distributed in the sample. The more frequent occurrence of such stacking faults, with increasing *n* value, leads to a somewhat disordered layer stacking sequence.

Keywords: Perovskites; crystal structure; electron microscopy

1. Introduction

$Sr_2[Sr_{n-1}Ti_nO_{3n+1}]$ series (ST) represents the prototype of a huge family of layered oxides described by Ruddlesden and Popper about 50 years ago. This structural type is constituted by $[A_{n-1}B_nO_{3n+1}]$ perovskite-like blocks *n* octahedra thick, interleaved with A cations along one of the cubic directions of the perovskite, yielding phases with the general formula $A_2[A_{n-1}B_nO_{3n+1}]$ where $1 \leq n \leq \infty$ [1,2]. Ruddlesden-Popper compounds (RP) constitute one of the most important families of layered perovskites owing to various properties of fundamental and technological interest such as ion-exchange and intercalation [3], ion conductivity [4], catalysis [5] and magnetic properties [6] among others. In the case of ST, the upper member of the series is the well know $SrTiO_3$ perovskite (ST0, $n=\infty$), whose electrical behaviour changes from a high dielectric constant insulator to a metallic superconductor when doped with a variety of elements [7]. Furthermore, properties can also be modified by the variation of the SrO/TiO_2 ratio and the prospect of "engineering" the properties of the compounds by varying the value of *n* has stimulated experimental research as well as theoretical studies of several members of the ST series [8-12].

From the point of view of the synthesis, mechanosynthesis allows us to obtain the two ends of the series (n=1, Sr_2TiO_4 and n=∞, $SrTiO_3$), as nanometric powders, by direct reaction between SrO and TiO_2 during the mechanochemical activation process at room temperature [13,14], but in the case of the n=2-4 members, a subsequent thermal treatment was needed. $Sr_3Ti_2O_7$ (n=2) could be easily prepared as a single phase after annealing at temperature as low as 800 °C [15], but members with n=3 ($Sr_4Ti_3O_{10}$) and 4 ($Sr_5Ti_4O_{13}$) could not be isolated [13].

This work reports on a subsequent detailed microstructural investigation has been carried out using electron microscopy methods in order to investigate the existence of intergrowths, very common in this type of compound, of other members of the series in the compositions $Sr_3Ti_2O_7$, $Sr_4Ti_3O_{10}$ and $Sr_5Ti_4O_{13}$ after the thermal treatment of the mechanochemically activated powders.

2. Experimental

The synthesis procedure for $Sr_2[Sr_{n-1}Ti_nO_{3n+1}]$ (with n=1-4 and ∞) from a stoichiometric mixture of SrO and TiO_2 by a mechanochemical activation route has been reported in a previous work [13]. To isolate each stable phase corresponding to n=2-4, the mechanically activated precursors were heated in a furnace to temperatures between 600 °C and 1300 °C for different holding times, using a heating rate of 10 °C min^{-1}. The thermal treatments were finished by quenching in air. The samples were characterised using X-ray diffraction with a Siemens D-501 diffractometer (λ=1.5418 Å); the patterns were collected in the 2θ range of 5-60°, with scan rates of 0.05 °/s.

In the experiments reported here, the microstructural investigation of the milled powder after thermal treatment was carried out by HREM and selected area electron diffraction (SAED) for the compositions with $2 \leq n \leq 4$. For transmission electron microscopy studies, portions of each sample were crushed in an agate mortar and suspended in n-butanol. After ultrasonic dispersion, a droplet was deposited on a copper grid supporting a perforated carbon film. HREM images and SAED patterns were recorded using a Philips CM200 Ultra-Twin transmission electron microscope (TEM) operated at 200kV and a JEOL 3010 TEM operated at 300 kV. HREM images were recorded at moderate values of underfocus (typically close to Scherzer defocus) are primarily interpreted in terms of periodicity and not in terms of absolute atom locations; for this reason full image simulations were unnecessary. Nevertheless, in one case, an image simulation was performed using EMS On Line [16].

3 Results and discussion

Figure 1 shows the XRD patterns of the final products of the mechanochemically activated powders (n+1)SrO:$n$$TiO_2$ corresponding to n=2, 3 and 4 after the annealing at 1300 °C for 12 hours. The mean peaks of each phase are shown in the Figure 1. $Sr_4Ti_3O_{10}$ and $Sr_5Ti_4O_{13}$ could not be isolated as single phases, even after a heat treatment at 1300 °C, whilst $Sr_3Ti_2O_7$ was obtained as a pure crystalline phase at a temperature as low as 800 °C, when annealed for 24 hours. However, the presence of disorder in the stacking of the $[A_{n-1}B_nO_{3n+1}]$ blocks and A cations is not unusual in RP phases and it is not always possible to detect this by powder XRD. Therefore, a careful microstructural study on these layered phases is advisable.

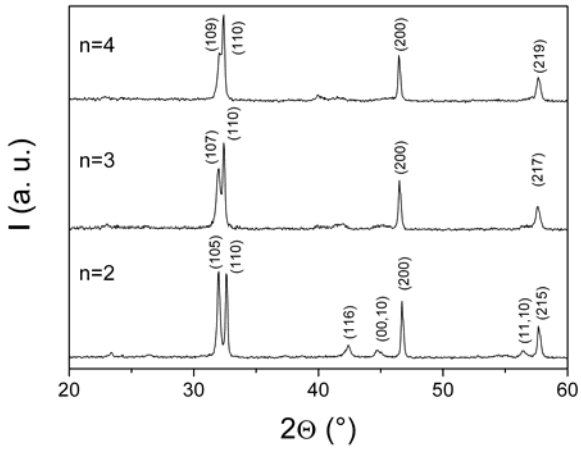


Figure 1

TEM studies of the $Sr_3Ti_2O_7$ showed well-ordered diffraction patterns corresponding well to expectations for this phase, as shown in Figure 2a. HREM images also frequently corresponded to regular n=2 ordering; this is exemplified by Figure 2b showing a well-ordered material with a regular spacing along the c-axis of between 9.9 and 10.2 Å, which corresponds to half of the c-parameter of the $Sr_3Ti_2O_7$ phase (SG I4/mmm, a= 3.9026 Å and c=20.372 Å). This 10 Å spacing corresponds to half a n=2 unit cell, and this makes sense since the structure along the c-axis is of two shifted but identical blocks of atoms. Although a single, ordered phase is dominant in this n=2 sample, a few intergrowths of other $Sr_2[Sr_{n-1}Ti_nO_{3n+1}]$ compounds can be observed along the c-axis (Figure 2b). These are sufficiently

uncommon, however, that they do not give rise to any significant reflections in XRD or electron diffraction patterns and the average spacing along the c-axis clearly corresponds to expectations for *n*=2.

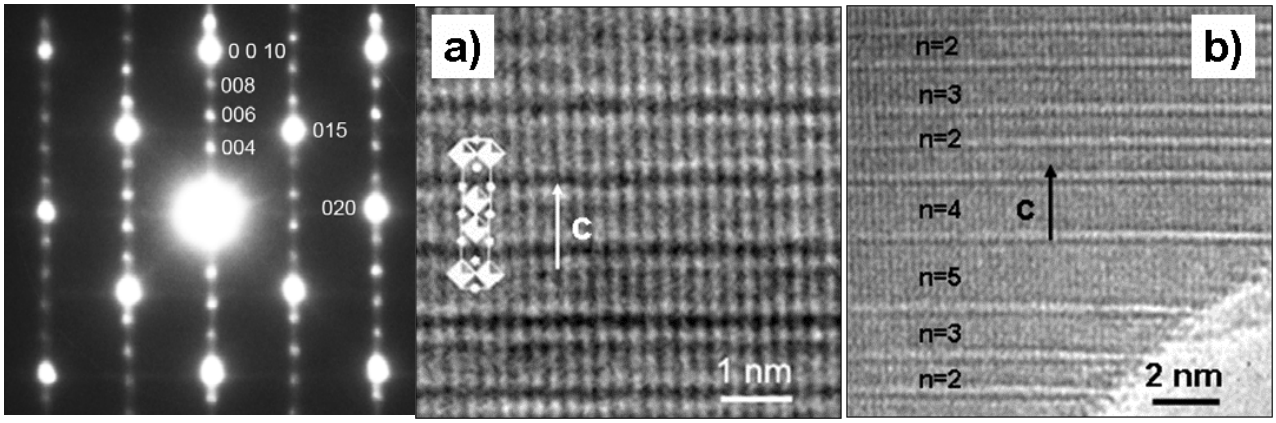


Figure 2: TEM images of the $Sr_3Ti_2O_7$ specimen: a) [100] SAED pattern; b) HREM of a well-ordered area with a regular spacing corresponding to the n=2 phase; c) HREM of a less well ordered area containing intergrowths of other n values.

Similar investigations have been carried out in the case of the *n*=3 and *n*=4 compositions. Figure 3a depicts a SAED pattern corresponding to the nominal composition $Sr_4Ti_3O_{10}$; this pattern corresponds well to modelled patterns for the tetragonal ST phase with *n*=3 (S. G. I4/mmm, a=3.9 Å and c=28.1 Å) viewed in the direction of the [110] zone axis. Nevertheless, significant streaking between the spots in the c-direction is apparent, which may indicate disorder along this direction. These conclusions was corroborated by the HREM study of the phase (Figure 3b); many *n*=3 layers are seen and the contrast is in reasonable agreement with image simulations (inset). Nevertheless, intergrowths of Ruddlesden-Popper layers (a half unit cell in thickness along the *c* direction) with *n* values other than the nominal one are in this case more frequent than in the $Sr_3Ti_2O_7$ composition. These results are in good agreement with those obtained by the X-ray diffraction studies.

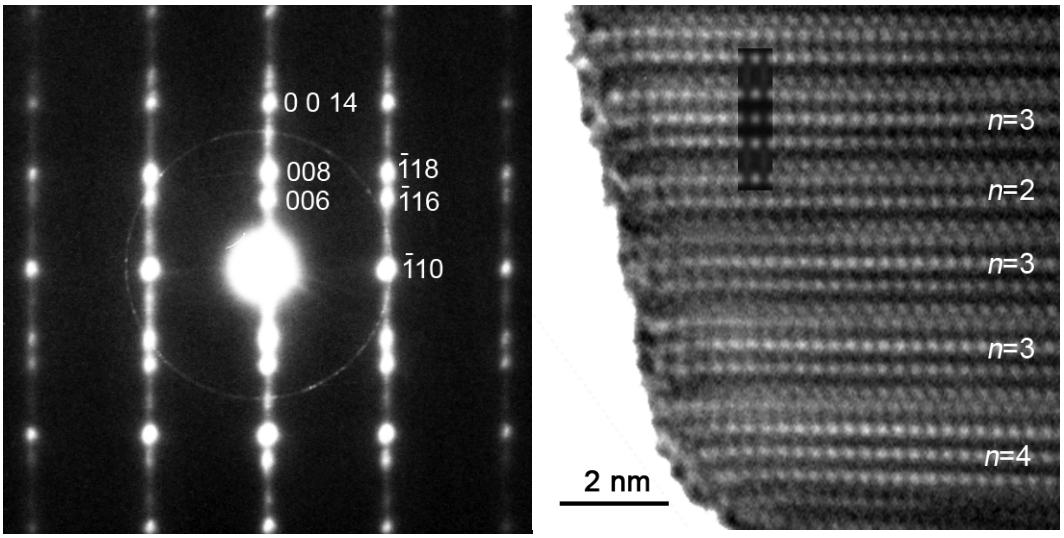
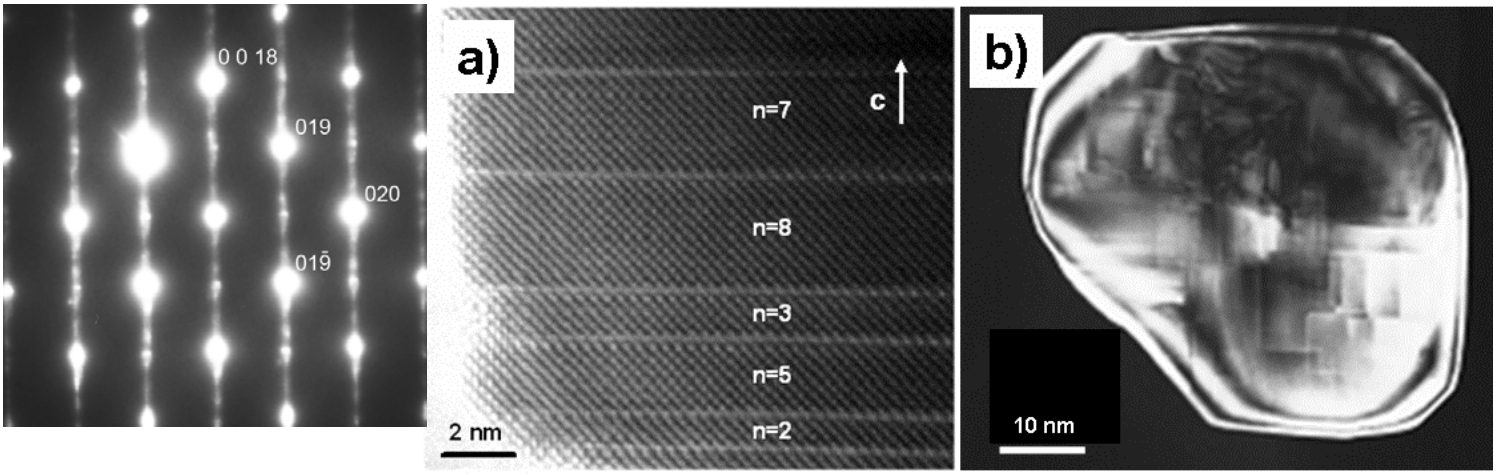


Figure 3: TEM studies of the $Sr_4Ti_2O_{10}$ phase: a) [110] SAED pattern; b) [110] HRTEM image showing mainly n=3 layers and a reasonable match to a simulated image.

Figure 4a shows a [100] SAED pattern from the $Sr_5Ti_4O_{13}$ sample; it is more difficult here to distinguish individual spots in the [001] direction and extensive streaking is present in this direction, suggesting that this material is less ordered than the *n*=2 and 3 materials. This is perfectly illustrated by the HREM image of Figure 4b, where no regions corresponding to *n*=4 can be observed. In an ordered ST phase, the Sr cation layers would occur perfectly periodically and would always be parallel to the (001) plane, as it can be observed in the micrograph of the Figure 2a. According to W. Tian *et al.* [9], the intergrowths in samples prepared by high temperature synthesis methods occur due to the absence of sufficient thermodynamic driving force (ΔG) for the formation of a single-phase, ordered RP structure. This effect seems to be more important for the higher *n* members and suggest that their free energies are not as low as a random mixture of $Sr_2[Sr_{n-1}Ti_nO_{3n+1}]$ layers. The results of this work confirm these conclusions about the thermodynamic stability of the ST phases, as can be clearly observed by comparison of the micrographs corresponding to *n*=2 (Figure 2a), *n*=3 (Figure 3) and *n*=4 (Figure 4a).

Figure 4. : TEM investigations of a nominally $Sr_5Ti_4O_{13}$ sample: a) [100] SAED pattern b) [100] HREM micrograph of the sample corresponding to a nominally $Sr_5Ti_4O_{13}$ composition and c) delete c).



4. Conclusions

$Sr_2[Sr_{n-1}Ti_nO_{3n+1}]$ phases with *n*=2-4 obtained by a mechanochemical activation route have been investigated by transmission electron microscopy techniques. The HREM investigation shows that all the samples exhibit a certain quantity of intergrowths of other ST members, even in the case of the apparently pure phases (by XRD characterization), as for example in the case of the nominally $Sr_3Ti_2O_7$ compound. This frequency of defects increases with the *n* value, in agreement with previous thermodynamic data.

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References

[1] Ruddlesden S, Popper P. Acta Crystallogr 1957;10:538-9.

[2] Ruddlesden S., Popper P. Acta Crystallogr 1958;11:54-5.

[3] Tahara S, Ichikawa T, Kajiwara G, Sugahara Y. Chem Mater 2007;19:2352-8.

[4] Prado F, Mogni L, Cuello GJ, Caneiro A. Solid State Ionics 2007;178:77-82.

[5] Ko YG, Lee WY. Catal Lett 2002;83:157-60.

[6] Schupp B, Dorr K, Ruck K, Nenkov K, Muller KH, Krabbes G.. Solid State Sci 2005;7:17-23.

[7] Wang YX, Zhong WL, Wang CL, Zhang PL. Solid State Commun 2001;120:133-6.

[8] Haeni JH, Theis CD, Schlom DG, Tian W, Pan XQ, Chang H, Takeuchi I, Xiang XD. Appl Phys Lett 2001;78:3292-4.

[9] Tian W, Pan XQ, Haeni JH, Scholm DG., J. Mater. Res. 16 (2001) 2013-26.

[10] Gutmann E, Levin AA, Reibold M, Muller J, Paufler P, Meyer DC. J Solid State Chem 2006;179:1864-9.

[11] Fennie CJ, Rabe KM. Phys Rev B 2003;68:Art. No. 184111.

[12] Noguera C. Phil Mag Lett 2000;80:173-80.

[13] Hungria T, Hungria AB, Castro A. J Solid State Chem 2004;177:1559-66.

[14] Hungria T, Algueró M, Hungria AB, Castro A. Chem Mater 2005;17:6205-12.

[15] Hungria T, Lisoni JG, Castro A. Chem Mater 2002;14:1747-54.

[16] Stadelmann, P and Jouneau, P-H, 1998, EMS On Line, available at http://cecm.insa-lyon.fr/CIOL/.